ELECTRICAL CONDUCTIVITY OF CONCENTRATED PHOSPHORIC ACID FROM 25° TO 60°C.

by Theodore Wydeven

National Aeronautics and Space Administration
Biotechnology Division
Ames Research Center
Moffett Field, California

The work of Greenwood and Thompson[1] called attention to a slow decrease in the electrical conductivity of freshly melted orthophosphoric acid. This was attributed to the slow orthophosphoric-pyrophosphoric acid interconversion at room temperature which lowered the concentration of the anomalously conducting dihydrogen phosphate ion. In conjunction with kinetic studies[2] on the interconversion, it was shown that a sample of orthophosphoric acid decreased in electrical conductivity by approximately 9.2% after melting at 45°C. EMF and cryoscopic measurements[3] have further shown that the concentration of pyrophosphate ion in equilibrated samples of stoichiometric orthophosphoric acid equals 0.28 molal at 38°C.

(1)N. N. Greenwood and A. Thompson, J. Chem. Soc. (1959), 3485.

(2)R. A. Munson, General Electric Co. Report No. 64-RL-(3820C), Research Laboratory, Schenectady, New York, 1964.

(3)R. A. Munson, J. Phys. Chem. 68, 3374 (1964).

Several reports on the electrical conductivity of concentrated phosphoric acid have appeared in the literature.[4,5,6] However, in view of a) the variability of reported conductivity values and b) the slow orthophosphoric-pyrophosphoric acid interconversion, the electrical conductivity of concentrated phosphoric acid has been redetermined over a wide range of concentration at intervals from 25 to 60°C.

(4)F. A. Keidel, Anal. Chem. 31, 2043 (1959).

(5)G. P. Kakulin and I. G. Fedorchenko, Russ. J. Inorg. Chem. (Eng. Trans.) 7, 1289 (1962).

(6)Monsanto Chemical Co., Tech. Bull. No. I-239, St. Louis, Missouri.

EXPERIMENTAL

Acid samples in the range 64.08 to 73.61 weight % phosphorus pentoxide were prepared by the thermal dehydration of analytical reagent grade "85%" phosphoric acid (62.14% phosphorus pentoxide by analysis in this laboratory) at about 150°C. Samples more concentrated than 73.61% P_4O_{10} were prepared by the slow addition of reagent grade P_4O_{10} to a thermally dehydrated acid sample containing approximately 70% P_4O_{10}. Since concentrated phosphoric acid attacks glass above 200°C., the sample vessel was placed in an ice bath during the addition of P_4O_{10} to prevent a large temperature rise. Samples prepared by the addition of P_4O_{10} were finally heated to 180°C. to hasten dissolution of the oxide. Samples ranged from a transparent, colorless liquid at the lower concentrations, to a straw yellow color at the higher concentrations.

A Washburn conductivity cell with platinized platinum electrodes, maintained at a constant temperature (±0.05°C.), was used in measuring the conductivity. Resistance was measured with an impedance bridge. Bridge balance was determined by either an oscilloscope or the impedance bridge null detector. No difference in resistance, within experimental error, could be detected by using either the oscilloscope or the null detector. (The manufacturer's estimate for the accuracy of the resistance reading is ±1%.) The accuracy of the bridge was further checked by measuring the conductivity of potassium chloride solutions and comparing the conductivity data with values found in the literature. See Table I.

Following the conductivity measurements, three samples of acid were taken for analysis. The acid concentration was determined by titration with sodium hydroxide using an expanded scale pH meter to detect the first equivalence point.

RESULTS AND DISCUSSION

In Table II values for the specific conductivity of phosphoric acid (62.14 to 85.58 weight % phosphorus pentoxide) from 25 to 60°C. are shown. The uncertainty in the concentration is expressed as the standard deviation. Specific conductivity isotherms vs. weight % phosphorus pentoxide in water are shown in Figure 1.

There is good agreement between Munson's[3] value of 4.596×10^{-2} ohm^{-1} cm^{-1} at 25°C. for the specific conductivity of an equilibrated sample of 100% phosphoric acid (72.43% phosphorus pentoxide) and the value 4.60×10^{-2} ohm^{-1} cm^{-1} at 25°C. taken from the curve in Figure 1. The good agreement

between the two studies at 25°C., where an equilibrium concentration of acid species would be more difficult to attain than at the higher temperatures, suggests that the samples in this work were equilibrated (within experimental error) in the region of 100% phosphoric acid.

At the higher acid concentrations, the deviation of experimental points from the curve is greatest (Figure 1). This might be attributed to one or more factors: a) a small deviation from an equilibrium concentration of acid species b) larger error in acid analysis due to moisture pickup from the atmosphere c) impurities introduced by phosphorus pentoxide that are not present in 85% phosphoric acid. These factors are discussed below.

Studies were carried out to determine if the conductivity at high acid concentrations was changing with time due to a slow approach to equilibrium. The conductivity of a sample containing 83.77% phosphorus pentoxide was monitored for 30 hours with the sample temperature maintained at 60 ±0.05°C. No change in resistance, within experimental error, was observed. The conductivity of the same sample was then monitored for 2 weeks at 25 ±0.05°C. with no change observed. These results suggest that even at the highest concentrations studied in this work the samples were equilibrated.

The standard deviation in acid concentration does not reflect a greater uncertainty in the analysis at the higher concentrations as compared to the uncertainty at lower concentrations.

Reagent grade phosphorus pentoxide was used in this work without further purification. Therefore, a small error in conductivity, at acid concentrations greater than 73.61% phosphorus pentoxide, might have been caused by a trace of impurity in the oxide. This error would not be

consistently high or low since the acid concentration prior to adding the oxide was only approximately 70% phosphorus pentoxide.

Shown in Table III are some representative values obtained by others[4,5,6] for the conductivity of phosphoric acid. The values found in this work are consistently higher than the values reported by Kakulin and Fedorchenko[5] and in Technical Bulletin I-239.[6] However, values found in this work are lower than those of Keidel.[4] The limited amount of experimental detail regarding sample preparation, analysis, and thermal history in the three reports cited does not allow for a critical comparison with this work.

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TABLE I: Comparison of Specific Conductivity Data for Potassium Chloride

Concentration in grams of KCl per 1000 grams of solution	Temperature, °C.	Specific Conductivity (ohm^{-1} cm^{-1})	
		This work	Jones, et al.[a]
0.7453	0	0.000774	0.0007736
7.4191	0	0.00711	0.007137
7.4191	25	0.0128	0.01286

[a]G. Jones and B. C. Bradshaw, J. Am. Chem. Soc. 55, 1780 (1933).

TABLE II: Specific Conductivity of Concentrated Phosphoric Acid

Concentration in weight % P_4O_{10}	Specific conductivity (ohm^{-1} cm^{-1}) at temperature (°C.)				
	25.0°	30.0°	40.0°	50.0°	60.0°
62.14±0.08	0.0888	0.102	0.134	0.167	0.202
64.08±0.04	0.0801	0.0928	0.122	0.154	0.189
65.58±0.06	0.0734	0.0858	0.114	0.146	0.180
67.89±0.16	0.0641	0.0756	0.102	0.131	0.165
70.31±0.11	0.0535	0.0639	0.0870	0.115	0.145
72.25±0.13	0.0447	0.0534	0.0740	0.0975	0.124
73.61±0.08	0.0355	0.0432	0.0606	0.0814	0.106
75.64±0.17	0.0210	0.0262	0.0389	0.0550	0.0744
77.33±0.11	0.0115	0.0148	0.0234	0.0346	0.0490
80.03±0.04	0.00336	0.00471	0.00855	0.0141	0.0220
81.50±0.06	0.00175	0.00256	0.00495	0.00855	0.0137
83.77±0.14	0.000860	0.00125	0.00245	0.00429	0.00699
85.58±0.09	0.000183	0.000282	0.000597	0.00108	0.00183

TABLE III: Comparison of Specific Conductivity for Concentrated Phosphoric Acid

Concentration in weight % P_4O_{10}	Temperature, °C.	Specific conductivity (ohm^{-1} cm^{-1})			
		This work	Kakulin, et al.[5]	Ref. 6	Keidel[4]
65	40	0.114	0.0979	0.104	(a)
70	40	0.0899	0.0792	0.078	- - -
75	40	0.0452	0.0216	0.035	- - -
75	50	0.0638	0.0308	(b)	0.071
80	50	0.0149	(c)	- - -	0.016
85	50	0.00186	- - -	- - -	0.0039

[a]No data reported for 40°C. [b]No data reported for 50°C. [c]Data reported for the concentration range 65.2 to 75.4 weight % P_4O_{10}.